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PATENT APPLICATION
Attorney's Docket No.: 2751.2001-000

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Christopher J. Nagel	
Application No.:	09/416,720	Group: 1751
Filed:	October 13, 1999	Examiner: Kopec, Mark T.
Confirmation No.:	6543	
For:	COMPOSITION OF MATTER TAILORING: SYSTEM I	

CERTIFICATE OF MAILING
I hereby certify that this correspondence is being deposited with the United States Postal Service with sufficient postage as First Class Mail in an envelope addressed to Assistant Commissioner for Patents, P.O. Box 2327, Arlington, VA 22202
on 12.19.02 [signature]
Date Signature
Danielle G. Lamkin
Typed or printed name of person signing certificate

DECLARATION OF CHRISTOPHER J. NAGEL UNDER 37 C.F.R. 1.132

Assistant Commissioner of Patents and Trademarks
P.O. Box 2327
Arlington, VA 22202

Sir:

I, Christopher J. Nagel, of Wayland, MA, declare and state that:

1. I am an inventor of the subject matter described in U.S. Serial No. 09/416,720, claiming a manufacturing copper and a method of preparing said copper. This patent application

was filed on behalf of Atomic Ordered Materials, LLC, 421 Currant Road, Fall River, Massachusetts 02720.

2. I have thoroughly studied the above-identified application and the Office Action mailed from the Patent Office on July 22, 2002. The Examiner states that Claims 103 and 104 are rejected as being unpatentable over Ishida, *et al.* (U.S. Patent No. 5,308,379; hereinafter "the '379 Patent") or Japanese Publication No. 4-99236. The Examiner states that the '379 Patent discloses an extra low oxygen copper that is produced by a melt process where graphite is present and reducing gases are added. The Examiner states that JP 7-99236 discloses an extra low oxygen copper produced by mixing nitrogen, argon and/or carbon monoxide with a molten metal. The Examiner asserts that although the instant method and the methods disclosed in the cited references are not identical, the resultant copper products would be identical. The Examiner states that the burden for overcoming the cited references is to present evidence establishing an unobvious difference between the claimed product and the prior art products.

3. I have performed extensive research in the metallurgical arts. I received a B.A. in Chemical Engineering from Michigan Technological University and a D.Sc. in Chemical Engineering from the Massachusetts Institute of Technology. In addition, I have been employed by the United States Steel Corporation Gary Works (Gary, Indiana) and Molten Metal Technology, Inc. (Waltham, Massachusetts). The results of my work are disclosed in numerous patents. Examples of such patents include U.S. Patents Nos. 5,640,706, 5,640,707, 5,640,709, 5,679,132, 5,717,149, 5,744,117, 5,776,420, 5,866,095, 6,096,109 and 6,258.988. In particular, I am familiar with the properties and behavior of metals or alloys near or above their melting points, and after they have subsequently re-solidified.

4. Metal compositions prepared by the method of the instant application have unexpected properties, as compared to metal compositions prepared by conventional methods. Novel properties include changes in color, luster, hardness, magnetism, as well as in the x-ray fluorescence spectrometry signature typically associated with those metals. Additional data related to novel properties of metal compositions prepared by the instant method can be found in U.S. Serial No. 10/123,028, filed April 12, 2002.

5. Differences have been demonstrated between manufactured copper and extra low oxygen copper (ELOC), manufactured in exact accordance with Example 1, sample of invention Nos. 2 of U.S. Patent No. 5,308,379, via a two fold approach:

1) On behalf of Atomic Ordered Materials (AOM), myself and others working under my direction have reproduced the patent material and through independent party testing has validated significant differences in the physical properties of the ELOC and manufactured copper. Manufactured copper refers to copper that has been prepared according to the instant method.
2) Through a third-party, the original inventors (U.S. Patent 5,308,379) have been contacted and the differences in physical properties have been confirmed.

Criteria for Comparison

In order to validate the differences between ELOC and manufactured copper, a mechanism was developed that:

1) Allowed ready comparison of the two materials through clear metrics.
2) Measured ubiquitous changes in the manufactured copper that were significantly different from the properties of ELOC and/or non-processed copper. Non-processed copper refers to copper that has not been prepared by the method of the '379 Patent or an equivalent method or by the method disclosed in the instant application.
3) Depended on data readily available in the public domain (i.e., typically straight-forward, low cost analyses, not considered proprietary) or data that could be readily gathered from reproducing the method of the '379 Patent.

Several metrics were identified to demonstrate the controlled physical property changes observed in the new composition of matter. For example, some physical properties that fit the criteria above include, but are not limited to, hardness, magnetic character changes, variations in

color, and characteristic changes in the XRF spectra. The table below highlights the data that will be presented in this document.

Table 1: Composition of Matter Changes Evidenced by Major Changes in Physical Properties

	Physical Properties Manipulated		
	Non-Processed Copper	**Extra-Low Oxygen Copper**	**Manufactured Copper**
Color	Copper	Copper	Red
Lustre	Metallic	Metallic	Glassy/Metallic
Hardness (Rockwell F)[1]	N/A	25	43
Magnetism	None	None	• Ferromagnetism: attraction to iron filings (or powder) • Magnetic attraction: neodymium iron boron magnetic attraction
XRF	N/A	Standard	• $K_{\alpha_{1,2}}$ centroid shift • $K_{\alpha_{1,2}}$ scans are anisotropic axial to radial • $K_{\alpha_{1,2}}$ S peak increase relative to starting material

Data Documentation

U.S. Patent 5,308,379 Inventor's Statement

Through a third-party consultant the original inventor, Norikazu Ishida was contacted at the Sakai plant of Mitsubishi Materials Corporation. Hardness, density, XRF analyses, and other physical property data were requested. The inventor's response is below (See Attachment 1):

> *"Since we [sic] the issuance of patent 5,308,379 we have not followed this research so there is no new data or information that we can offer. We do not produce extra-low oxygen-free copper (<0.5 ppm) at this time but we do manufacture OFC with an oxygen content of about 1 ppm on a commercial basis. The*

[1] Rockwell Hardness F scale using 1/16" ball and 60 kgf.

material has essentially the same properties as the extra-low oxygen-free copper."[2]

Given that the inventor specified that the physical properties of the patent material were "essentially the same" as the commercially available OFC material with <1 ppm oxygen, the properties of Mitsubishi's commercial Class 1 F-68 (<1 ppm oxygen) material were investigated.

Attachment 2, taken directly from the Mitsubishi Materials website[3], shows a tabulation of typical physical properties of the OFC copper which the inventor has stated are representative of the material produced by the method of the '379 Patent. Table 2 below compares the physical properties of the '379 Patent copper to that of non-processed copper. No significant difference exists between the material produced by the method of the '379 Patent and non-processed copper. Hence, the physical properties of the copper material generated by the method specified in the '379 Patent are within the domain of the composition of matter characterized by non-processed natural copper.

Table 2: Copper Prepared By The Method of The '379 Patent Has the Same Properties as Non-processed Copper

Material Property	OFC Class 1 F-68	Non-processed Copper
Density g/cm^3 (293K)	8.93	8.92
Melting Point (K)	1356	1357.7
Thermal Conductivity (J/cm-sec-K) 293K	4.03	4.01
Volume Resistance $\mu\Omega cm$ (293K)	1.685	1.673
Linear Expansion Modules 10^{-6} (293-393K)	17.1	16.6
Young's Modules 10^5MPa	1.18	1.30
Rigidity 10^5MPa	0.44	0.48
OFC properties as reported by Mitsubishi Materials; Non-processed Copper properties as reported by The Artificial Intelligence Laboratory at the Massachusetts Institute of Technology, www.ai.mit.edu/people/tk/tks/copper.html and Webelements, www.webelements.com, Mark Winter, The University of Sheffield.		

Reproduction of ELOC material

To provide further evidence of fundamental differences and distinctions between the manufactured copper of the subject application and the ELOC of the '379 Patent, we replicated

[2] From Ishida Norikazu (noishida@mmc.co.jp) through Craig J. Craven (ccraig@mmc.co.jp) and copied to Hori Kazumasa (horik@mmc.co.jp) and Kakimoto Akihiro (akkmt@mmc.co.jp), dated Friday, September 13, 2002 at 3:52 am.

[3] www.mmc.co.jp/sakai/enu/products/ofcclass.htm.

09/416,720

Example 1, sample of invention Nos. 2 of the '379 Patent. The process and experimental program outlined in the patent were followed explicitly. For unspecified items, such as casting, heating/cooling rate, or lance injection mode (e.g., bubbling versus jetting), an expert of extraordinary skill in the art was consulted. Prof. Merton C. Flemings, Ph.D.[4], former Chair of the Materials Science and Engineering Department of the Massachusetts Institute of Technology (MIT), Toyota Professor, and Director of the Materials Processing Center assisted with the development of the experimental program with respect to the unspecified conditions. Attachment 3 shows a run summary and the Standard Operating Procedures (SOP) from the demonstration.

A 15 kg ingot of Extra-Low Oxygen Copper was generated via the procedure outlined in the patent and delineated in Attachment 3. Described below is a detailed comparison of representative physical properties of non-processed copper, ELOC copper, and manufactured copper.

Color

Non-processed Copper Color

Only two of the naturally-occurring metals in nature are not silver in color, gold and copper. Non-processed copper's color is distinct. Shown to the left is a picture of a naturally-occurring copper nugget taken from a streambed in Minnesota (website: http://geology.about.com/library/bl/images/blcopper.htm). Because native copper corrodes fairly quickly at surface conditions, nuggets like this do not last long. Upon aging, copper will tarnish (due to oxidation) to a green patina.

[4] Prof. Merton C. Flemings earned his S.B., S.M., and Sc.D. in metallurgy from MIT and has served as a metallurgist at Abex Corporation. He has received the TMS Leadership award from the Minerals, Metals, and Materials Society, the Simpson Gold Medal from the American Foundry Society, and is a fellow of ASM International, TMS, and the Japan Iron and Steel Institute. He currently acts as a materials and metallurgy consultant to industry and is a renowned expert in non-ferrous and ferrous casting.

Extra-Low Oxygen Copper (ELOC) reproduced via U.S. Patent 5,308,379 Color

The ELOC ingot generated via the method described in U.S. Patent No. 5,308,379 exhibited the same color as non-processed copper, namely the distinct color of a copper penny. The slight black markings on the top of the ingot are caused by carbon deposits[5], that settled on the top (e.g., dross) during casting.

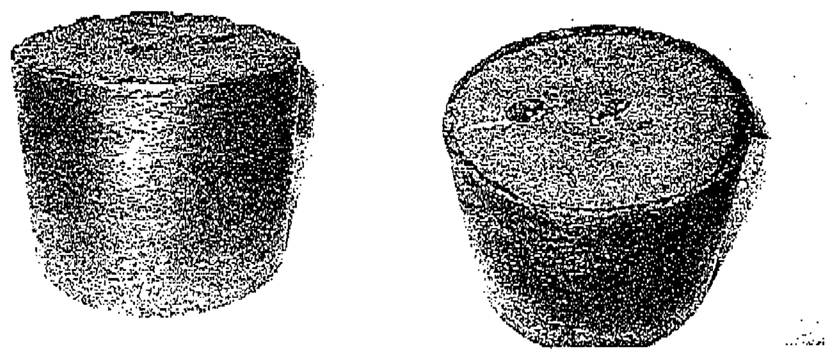
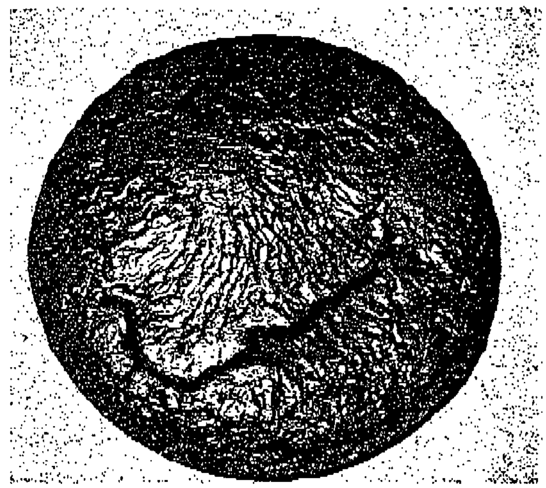


Figure 1: Extra-Low Oxygen Copper (ELOC) reproduced via U.S. Patent No. 5,308,379

Manufactured Copper Color

Through the method disclosed in the instant application, we have changed the color of elemental copper ($\geq 99.98\%_{wt}$) demonstrating a change in the composition of matter. Shown below are two images (views) from a manufactured copper run (14-00-03; Attachment 7, also disclosed in U.S. Serial No. 10/123,028), in which the color changed to an intense, deep red. In addition, a glass-like luster (non-processed copper has a metallic luster) was generated.

[5] ELOC patent specifications afford for the presence of carbon in the graphite crucible and the injected CO.



Note the distinct red color, as made apparent by the yellow highlighter, white paper, and black benchtop in the background of the left-hand image. This intense red color is not seen in naturally occurring copper. The top view shows the glassy luster, as opposed to the metallic luster exhibited by non-processed copper.

Comparison of Non-Processed, ELOC and Manufactured Copper Color

The ELOC we prepared exhibits the characteristic non-processed (natural) copper color, while the manufactured copper ingot is deep red. Shown below is a picture of the manufactured copper ingot from above (Run 14-00-03) side-by-side with the ELOC ingot (Run 14-02-07). While the manufactured copper is an intense red color (see reference visible spectrum in background), the ELOC is the color of non-processed copper. Thus, we have induced a color change in the manufactured copper, demonstrating that a new composition of matter has been prepared (

Table 3).

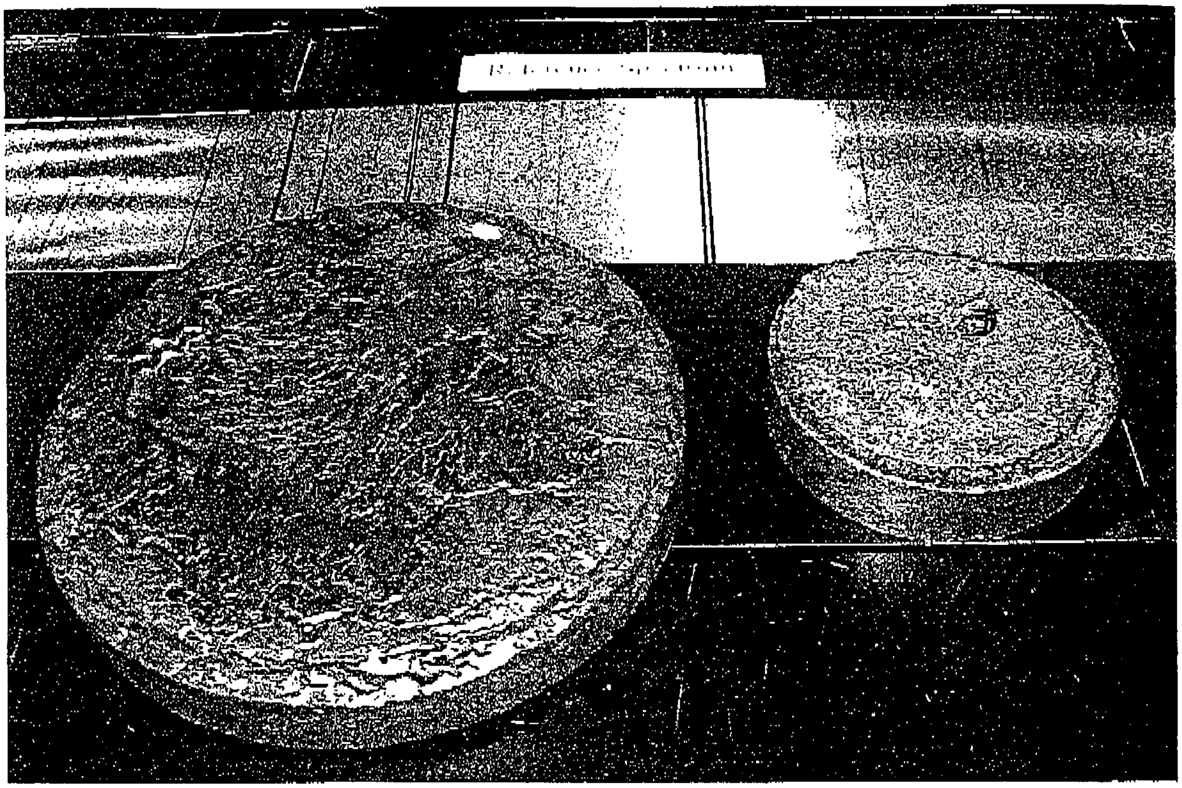


Table 3: Induced Color Change in Manufactured Copper

Physical Property: Color			
	Non-Processed Copper	**ELOC**	**Manufactured Copper**
Color	Copper	Copper	Red
Luster	Metallic	Metallic	Glassy/Metallic

Hence, the color of the ELOC ingot is the expected color of non-processed copper, but the manufactured copper is a deep, intense red, with a glassy (as opposed to metallic) lustre.

Magnetic Properties

Non-processed Copper Magnetism

Non-processed copper does not exhibit ferromagnetism; it does not attract iron filings, nor does it attract known magnets. Only five elements (iron, Fe; cobalt, Co; nickel, Ni;

gadolinium, Gd; and dysprosium, Dy) and their alloys exhibit ferromagnetism, a phenomenon in which exchange coupling is believed to occur between adjacent atoms, coupling their magnetic moments together in rigid parallelism. "*This is a purely quantum effect and cannot be explained in terms of classical physics. Modern quantum physics successfully predicts that this [phenomenon] will occur only for the five elements listed*".[6]

Hence, non-processed copper exhibits no special or unique magnetic properties.

<u>ELOC Magnetism</u>

Upon completion of the generation of the ELOC 15 kg ingot, a series of experiments were performed (identical to those performed on the manufactured copper) to identify any unique properties. The protocol included testing via three different methods:

<u>Magnetic attraction</u>: An 1/8" diameter neodymium iron boron magnet was scanned consistently and uniformly across the surface of the ingot to detect areas of attraction.

<u>Attraction to iron</u>: The attraction of iron filings (or powder) to specific points on the ingot were quantified by enumerating the number of filings retained on the ingot surface in a vertical or upside-down orientation.

<u>Gauss measurement</u>: The magnetic behavior of various points on the ingot (cross-sectional grid system) were quantified via the use of a F. W. Bell 4048 Gauss meter.

The ELOC exhibited no point attractions to magnets, no attraction to iron filings, and no Gauss readings. Moreover, no unique magnetic properties were stated by the patent inventor or by Mitsubishi Materials (see Attachments 1 and 2).

Hence, ELOC exhibits no unique or distinguishable magnetic properties, and is similar in behavior to non-processed copper.

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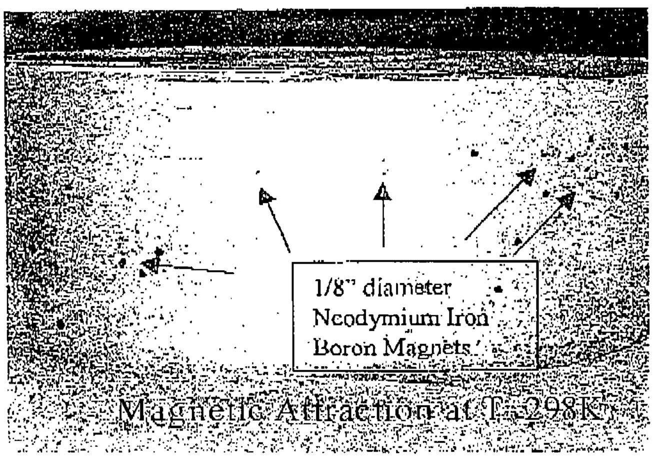
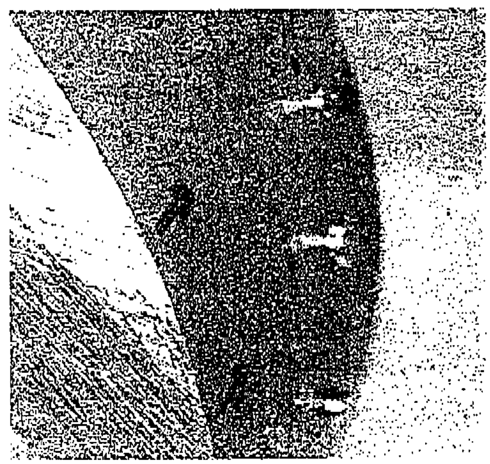
6 <u>Fundamentals of Physics</u>; David Halliday and Robert Resnick, John Wiley & Sons, Inc. ©1974, Sec. 33-5, p. 619.

Manufactured Copper Magnetism

Elemental copper (e.g. $\geq 99.98\%_{wt}$) manufactured via the procedure outlined in the instant application revealed magnetism[7]. Discrete magnetic points exhibited equivalent attraction to a neodymium iron boron magnet (1/8" diameter, see testing protocol above). The manufactured copper also exhibited magnetic point attraction to iron filings (or powder). This behavior, exhibited by the manufactured copper, is that which would be expected from a ferromagnetic material. The following pictures show the ferromagnetic behavior of the manufactured copper ingot.





These enlargements show actual 1/8" diameter neodymium iron boron magnets, attracted to the ingot from patent demonstration run 14-00-01 (Attachment 6, also disclosed in U.S. Serial No. 10/123,028).

Neither non-processed copper nor the reproduced ELOC exhibited any magnetic attraction.

[7] Multiple patent run demonstrations revealed magnetic properties in $>99.98\%_{wt}$ pure copper. The figures in this section are from patent demonstration run 14-00-01.

Table 4: Manufactured Copper Exhibits Magnetism Unlike ELOC or Non-processed Copper

Physical Property: Magnetism			
	Non-processed Copper	**ELOC**	**Manufactured Copper**
Magnetism	None	None	• Ferromagnetism[8]: attraction to iron filings (or powder) • Magnetic attraction: neodymium iron boron magnetic attraction

Hardness

Hardness is one of the physical characteristics commonly used to identify a material in its elemental state. Material hardness is believed to be controlled by the bond strength, character, and atomic coordination; cold working can affect hardness.

Both ELOC and manufactured samples were handled identically; neither the ingot developed via the '379 Patent method (to give "processed copper"), nor the ingot developed by the method of the instant application has been either rolled, cold worked, or the equivalent. That is, neither the processed or manufactured copper have been subjected to post process (cold) working.

Non-processed Copper Hardness

The data for the hardness of natural copper (non-worked) is unavailable and not relevant to this discussion. As most copper has been worked in some manner, the hardness data reported in the literature is for manipulated samples. For example, the simple act of cutting the copper, can work harden a local area. Hence, particular caution was taken in preparing the ELOC and manufactured copper ingots for testing (i.e., post cutting, the testing surface was polished to obtain consistent and accurate results).

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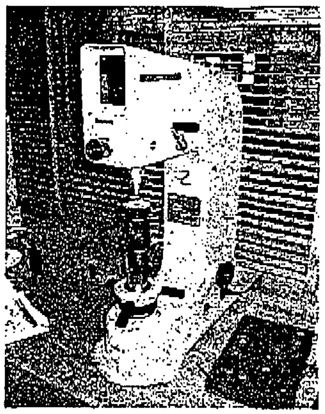
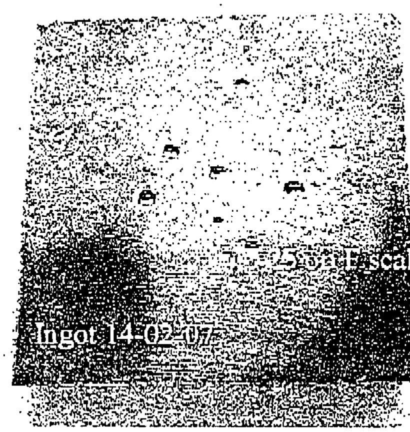
8 Modern quantum physics predicts ferromagnetism for five elements: Fe, Co, Ni, Gd, and Dy (Fundamentals of Physics, Halliday and Resnick).

ELOC Hardness

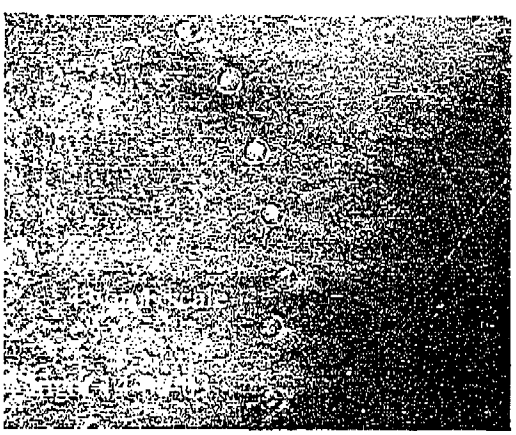


Hardness testing of the ELOC ingot was performed by Mark Jansen at the University of Massachusetts Dartmouth Mechanical Engineering Department (and overseen by Prof. Sherif D. El Wakil). The machine used for testing was an Officine Galileo Model A200 (shown at left). A standard Rockwell F test was performed with a 1/16" ball and 60 kgf.



The sample was tested in multiple locations, with a resultant hardness of 25 on the Rockwell F scale. To prepare the sample for testing, the copper ingot sample was etched. First the copper material was polished to between 3 µm and 6 µm. Then the ingot was submerged for 10 seconds in an etching solution consisting of 25 ml NH_4OH (ammonia), 25 ml 3% H_2O_2 (hydrogen peroxide), and 25 ml deionized H_2O. The sample was then rinsed in DI water. The picture at right shows the locations of the hardness sample testing for the ELOC.

Manufactured Copper Hardness



Via the same hardness testing methods as used on the ELOC (described above), and through the same independent party, we tested the hardness of the ingot prepared via the method outlined in the instant application (included in the attachments as Run 14-00-03). The ingot was tested at multiple locations, after etching in the manner described

above.

The resultant hardness was 43 on the Rockwell F scale. The standard deviation for the hardness testing was 1.5 (σ=1.46), hence the hardness results obtained for the ELOC copper and the manufactured copper were statistically, significantly different.

Table 5 below summarizes the hardness data obtained via third-party testing using the Rockwell F hardness scale.

Table 5: Manufactured Copper has Hardness Distinct and Different from ELOC and Non-processed Copper

	Physical Property: Hardness		
	Non-Processed Copper	**ELOC**	**Manufactured Copper**
Hardness (Rockwell F, 1/16" ball, 60 kgf)*	N/A**	25	43

* The standard deviation on the hardness testing was typically <1.5 with the greatest standard deviation being 3.5 (this data series had one outlying data point, skewing the statistics). In all cases the hardness of sample 14-02-07 (ELOC) was statistically, significantly less than the manufactured copper (14-00-03).

**All natural copper obtained by AOM had been cold worked in some fashion (e.g., pelletization). Hence, no natural copper sample was readily available that could be tested on an equivalent basis to the ELOC and manufactured copper.

Hence, the manufactured copper exhibits statistically significantly different hardness from the ELOC.

X-ray Fluorescence Spectrometry[9]

X-ray fluorescence spectrometry (see Attachment 4) was used to determine the electronic and quantum state character of the subject material. The copper used to produce both the ELOC and manufactured copper was extremely pure ($\geq$99.99 $\%_{wt}$ Cu and $\geq$99.98$\%_{wt}$ Cu, respectively) and low in sulfur (e.g., $\leq$ 7ppm). X-ray fluorescence spectrometry (XRF) analyses can verify changes in electronic character via spectral emission profiles and emission profile centroid shifts.

[9] X-ray fluorescence (XRF) spectroscopy provides qualitative identification and quantitative determination of an elemental composition (bulk). An X-ray tube is used to excite and remove an inner shell electron; the resulting vacancy is filled by an outer shell electron. The transition from outer shell to inner shell is accompanied by an X-ray photon emission whose wavelength is indicative of the energy difference and hence the element. Emission intensity is indicative of elemental concentration.

Non-processed Copper XRF

Naturally occurring (non-processed) copper is typically high in sulfur content due to the high solubility of sulfur in copper. Therefore, no XRF was performed on non-processed copper as the net result would be an XRF showing high quantities of sulfur, with no relevance to the present technical discussion.

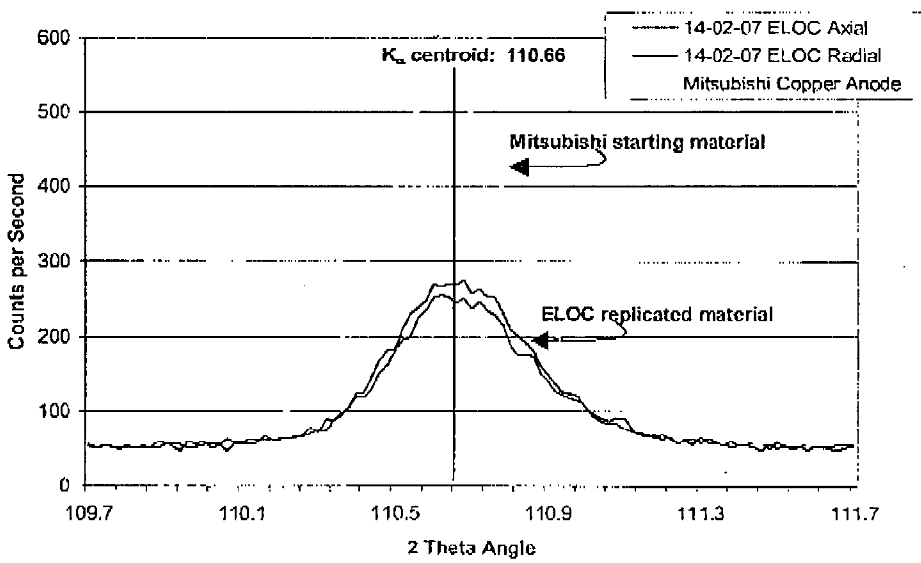


Figure 2: Sulfur $K_{\alpha_{1,2}}$ XRF Scans of the Replicated Mitsubishi Patent Material (ELOC)

ELOC XRF

XRF analysis was performed on both the starting ELOC material (electrolytic, oxygen-free copper) and the final Extra Low Oxygen Copper (ELOC) replicated product. XRF was performed by an independent party, Dirats Laboratories, using an ARL 9800XP Multichannel XRF Quantometer.[10] See Attachment 5 for sulfur $K_{\alpha_{1,2}}$ scan protocols.

[10] Dirats Laboratories is located at 41 Airport Rd. Westfield, MA. All XRF scans were performed in an identical manner using an incremental S-type scan, a Ge111 crystal, and an FPC detector. The scans were

The copper starting material for the production of ELOC was obtained from Mitsubishi Chemical using their oxygen-free copper anode material: "an electrolytic grade oxygen-free copper having an oxygen content less than 20 ppm"[11]; typically >99.98 $\%_{wt}$ Cu. Shown below is an XRF of the starting material (prior to processing) along with axial and radial scans of the ELOC product.

Minute amounts of sulfur were found in the starting material. As expected, the processing protocol, designed to manufacture ultra-pure copper, was successful in lowering the sulfur content uniformly in both the axial and radial directions.

Manufactured Copper XRF

XRF analysis was performed on both the starting material and the final manufactured copper product. XRF was performed by the same independent party, Dirats Laboratories, using the same analytical protocol used for the ELOC.

The copper chop starting material for the manufactured copper was obtained from Hickman, Williams, & Company, typically ≥99.98 $\%_{wt}$ Cu. Shown below is an XRF of the starting material (prior to processing) along with axial and radial scans of the manufactured copper product. Several different and unique results were obtained.

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performed through the angles 109.7 to 111.7 at increments of 0.02, with a counting time of 5 sec. The scans were performed in a vacuum environment using a fine collimator, with rotation, no PBF, and elliptical mask 2.

11 U.S. Patent No. 5,308,379 by Ishida (Mitsubishi); column 3; lines 13-14.

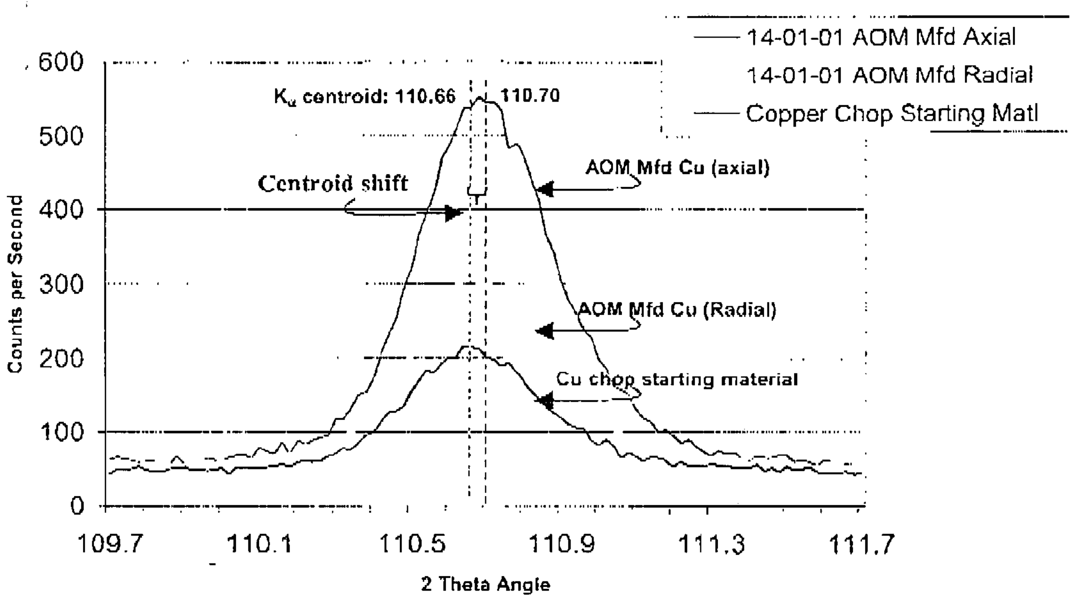

Figure 3: Sulfur $K_{\alpha_{1,2}}$ XRF Scans of manufactured copper product (AOM Mfd)

First, the sulfur content of the material showed an apparent increase, although the processing environment would be expected to strip sulfur. Sulfur was not input into the processing system and potential residual sulfur sources (e.g., graphite crucible) were held constant[12] between the ELOC and manufactured copper runs. Moreover, LECO analysis, a combustion-based analytical method followed by gas phase infrared SO_x detection, showed no corresponding increase in sulfur content, indicating that this result is strictly related to the electronic nature of the material[13]. Close inspection of the electronic spectra, reveals a $K_{\alpha_{1,2}}$ centroid shift, which is a measurement and expression of altered electronic character.

Second, the apparent increase in sulfur content is anisotropic, despite the use of a well-mixed system having extremely high sulfur solubility (~30 $\%_{wt}$). Directionally-dependent compositional changes are unexpected in a well-mixed, uniform, natural high purity elemental copper system. While not being bound by theory, anisotropic behavior is explainable if the

12 The crucibles used were the same grade and purity level, and purchased from the same manufacturer.

13 The manufactured copper has been changed such that the XRF results show an increase in sulfur content while actual sulfur composition stayed the same or decreased.

altered electronic character induces a type of long-range ordering that is detectable via XRF analysis.

Third, the instrument-calculated centroid (the analytically-predicted characteristic distribution center) for each of the starting materials was 110.66[14]. For the axial scan of the manufactured copper, the scan showed a 2½ fold increase in apparent sulfur concentration, the centroid shifted to the right, from a 2 theta angle of 110.66 to 110.70, which is an indication of the change in electronic character.

XRF Comparison of ELOC vs. Manufactured Copper

Identical procedures were performed by an independent party to perform XRF analysis on the starting materials and the ELOC and manufactured copper products. The following observations were made and quantified.

- The sulfur content of the ELOC starting material decreased as expected during the processing to create ultrapure copper (see Figure 2). The sulfur content of the manufactured copper showed an apparent increase despite the fact that there was no apparent source of sulfur and the processing conditions favored the removal of sulfur from the system (see Figure 3). While not being bound by theory, this apparent increase in the sulfur concentration detected by XRF (not detectable via combustion based analytical methods, such as LECO) may be explained by a change in the underlying electronic character of the material. The table below quantifies these changes.

[14] The actual peak is between 110.66 and 110.64; artifacts of interval sample collection can assign a sulfur $K_{\alpha_{1,2}}$ peak to 110.64.

XRF Sulfur $K_{\alpha_{1,2}}$ Analysis	Counts per Second (a measure of relative concentration)	% Change from Processing
Replicated ELOC:		
Starting Material	542.7	
ELOC Radial	252.4	-53.49%
ELOC Axial	267.8	-50.65%
Manufactured Cu (14-01-01):		
Starting Material	215.0	
Manufactured Radial	321.8	+49.67%
Manufactured Axial	543.8	+152.79%

- While the apparent decrease in sulfur for the ELOC product was uniform (as is expected in a well-mixed system, see Figure 2), the manufactured copper showed a directionally-biased concentration discrepancy (unexpected in a well-mixed system, see Figure 3). The anisotropic behavior of the manufactured copper is quantified in the table below:

XRF Sulfur $K_{\alpha_{1,2}}$ Analysis	Counts per Second (a measure of relative concentration)	% Change from Processing	Difference in % Change (axial to radial)	Isotropic vs. Anisotropic Behavior
Replicated ELOC:				
Starting Material	542.7			
ELOC Radial	252.4	-53.49%	2.84%	Isotropic
ELOC Axial	267.8	-50.65%		
Manufactured Cu (14-01-01):				
Starting Material	215.0			
Manufactured Radial	321.8	+49.67%	103.12%	Anisotropic
Manufactured Axial	543.8	+152.79%		

- Finally, the detected centroid (determined computationally via the XRF instrumentation) in the starting materials and in the ELOC product was consistently 110.66. However, the centroid for the manufactured copper product in the axial direction was 110.70 (see centroid shift in Figure 3), which statistically different from the expected value (110.64-110.66). The centroid shift is quantified below:

XRF Sulfur $K_{\alpha_{1,2}}$ Analysis	Counts per Second (a measure of relative concentration)	Centroid[15]
Replicated ELOC:		
Starting Material	542.7	110.64
ELOC Radial	252.4	110.64
ELOC Axial	267.8	110.66
Manufactured Cu (14-01-01):		
Starting Material	215.0	110.66
Manufactured Radial	321.8	110.66
Manufactured Mfd Axial	543.8	110.70

The XRF results from the ELOC processing were as expected, detecting very small quantities of sulfur that are uniformly removed via processing.

The combined sulfur $K_{\alpha_{1,2}}$ XRF analysis of manufactured copper reveals a change in the underlying composition of matter: (1) the apparent sulfur concentration increased[16] (although no source of sulfur existed and operating conditions favored sulfur removal); (2) the sulfur concentration increased in a directionally-dependent manner (i.e., anistropic change in an isotropic system), and: (3) a shifted sulfur $K_{\alpha_{1,2}}$ centroid.

[15] The actual peak is between 110.66 and 110.64; artifacts of interval sample collection can assign a sulfur $K_{\alpha_{1,2}}$ peak to 110.64.

[16] No changes in sulfur concentration were detected via LECO analysis.

Table 6: The XRF from Manufactured Copper is Distinct from ELOC Copper

Physical Property: XRF Spectra		
	ELOC Copper	**Manufactured Copper**
XRF $K_{a_{1,2}}$ S Spectra	**Expected**	**Unexpected**
Processing Concentration Change	**Decreased** (stripped during processing)	**Increased** (no S source; process favors decrease)
Uniformity of Concentration Change	**Isotropic**	**Anisotropic**
Centroid Shift	**10.64-10.66**	**10.66 to 10.70**

The detected shifts in energy levels and electronic states of the manufactured copper indicates a change in the composition of matter.

Conclusions

We have applied a scientifically defendable mechanism to demonstrate that the manufactured copper of the subject patent is significantly different from ELOC, and cannot be prepared by the methods disclosed in U.S. Patent No. 5,308,379.

1. We have contacted the inventor of the '379 Patent who stated that the physical properties of ELOC are not significantly different from "oxygen-free" copper, having less than 1 ppm oxygen.

2. We have reproduced ELOC and tested it, via independent parties. No significant physical property changes were observed to distinguish it from the starting material or "non-processed" copper.

3. We have demonstrated significant and unique electronic state and quantum character change, coupled to significant physical property change for the manufactured copper of the instant application.

Table 7 demonstrates a few representative examples of physical parameters that have been modified from those of non-processed copper. Note, in each case, the manufactured copper exhibits unexpected physical characteristics while ELOC's properties match those of non-processed copper.

Table 7: Composition of Matter Changes Evidenced by Major Changes in Physical Properties

Physical Properties Manipulated	Non-Processed Copper	Extra-Low Oxygen Copper	Manufactured Copper
Color	Copper	Copper	Red
Lustre	Metallic	Metallic	Glassy/Metallic
Hardness (Rockwell F)[17]	N/A	25	43
Magnetism	None	None	• Ferromagnetism: attraction to iron filings (or powder) • Magnetic attraction: neodymium iron boron magnetic attraction
XRF	N/A	Standard	• $K_{\alpha_{1,2}}$ centroid shift • $K_{\alpha_{1,2}}$ scans are anisotropic axial to radial • $K_{\alpha_{1,2}}$ S peak increase relative to starting material

6. Based on the differences in properties between manufactured copper, prepared by the method of the instant application and "non-processed" copper or extra low oxygen copper, the manufactured copper has properties that are unexpected. Section 5 demonstrates the differences in properties can be observed, for example, in the color, luster, hardness, magnetism and x-ray fluorescence spectra of manufactured copper.

7. I hereby acknowledge that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so

[17] Rockwell Hardness F scale using 1/16" ball and 60 kgf.

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made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Christopher J. Nagel, D.Sc.

December 19, 2002
Date

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Attachment 1: Email Contact with Inventor via Third Party

Previous | Next | Back to Messages Printable View - Full Headers

Delete | Reply | Reply All | Forward | as attachment Move to folder OK

This message is not flagged. [Flag Message - Mark as Unread]

From: "Bruce Chanenchuk" <chanenchuk@attbi.com> | This is Spam | Add to Address Book
To: "Jean Balch" <janalch@yahoo.com>
Subject: Fw: Extra Low Oxygen Copper
Date: Fri, 13 Sep 2002 14:21:50 -0400

What now???

----- Original Message -----
From: "Craig J. Craven" <craig@mmc.co.jp>
To: "Charles Chanenchuk" <[illegible]>
Cc: "[illegible] (E-mail)" <[illegible]>; "[illegible] (E-mail)" <[illegible]>; "Kamamoto Akihiro (E-mail)" <[illegible]>
Sent: Friday, September 13, 2002 [illegible]
Subject: Re, Extra Low Oxygen Copper

> Dear Dr. Chanenchuk,
> I apologize for the delay in responding and thank you for your interest in
> Mitsubishi Materials.
>
> Since the issuance of patent 5,508,[illegible] we have not followed this research
> so there is no new data or information that we can offer. We do not produce
> extra-low oxygen-free copper (<0.1ppm) at this time but we do manufacture
> OFC with an oxygen content of about 1 ppm on a commercial basis. This
> material has essentially the same properties as the extra-low oxygen-free
> copper. If you would like some of this material for your research please
> advise your specifications (sizes, amount, etc.) and we will respond quickly.
>
> Best regards,
>
> Craig J. CRAVEN for
> [illegible] DA
> Assistant Manager, Manufacturing Section
> Mitsubishi Materials Corp., Sakai Plant
>
> e-mail: [illegible].co.jp
> Web site: www.mmc.co.jp/sakai/
>
> -----Original Message-----

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Attachment 2:

Taken directly from the Mitsubishi Materials website:

www.mmc.co.jp/sakai/enu/products/ofcclass.htm.

- Microstructure after heat treatment

  The large grain size and lack of contamination of Class 1 (photo below left) is compared to Class 2-3 (photo below right).

100 μm

100 μm

Class 1 Microstructure   Class 2-3 Microstructure

Mitsubishi Materials Oxygen Free Copper (Typical)

Item	Class 1 F-68	Standard OF
Density g/cm^3 (293K)	8.93	8.93
Melting Point °K	1,356	1,356
Specific Gravity J/gK (293K)	0.385	0.385
Thermal Conductivity J/cm. sec. K (293K)	4.03	3.94
Electrical Conductivity %IACS (293K)	102.3	101.5
Volume Resistance μΩ cm (293K)	1.685	1.699
Linear Expansion Modules 10^{-6} (293-393K)	17.1	17.0
Young's Modules 10^5MPa	1.18	1.18
Rigidity 10^5MPa	0.44	0.44

Attachment 3: Reproduction of U.S. Patent 5,308,379 Copper (ELOC)

EXPERIMENTAL PROCEDURE FOR COPPER RUN

A cylindrical Graphite-based crucible of a 100 pound induction furnace reactor (Inductotherm) fitted with a 75-30R Powertrak power supply was charged with 15 kg copper (99.998% purity; 20 ppm oxygen) through its charging port. The reactor was fitted with a graphite cap. During the entire procedure, a slight positive pressure of argon (~0.5 psi) was maintained in the reactor using a continuous backspace purge. The reactor was heated to the metal charge liquidus point (1200°C), at a rate no greater than 300°F/hour, as limited by the integrity of the crucible. The induction furnace operated in the frequency range of 0 kHz to 3000 kHz, with frequency determined by a temperature-controlled feedback loop implementing an Omega Model CN300 temperature controller.

Upon reaching the target temperature of 1200°C a graphite nozzle was lowered into the molten copper bath. The graphite nozzle was flowing CO gas at a rate of 5 l/min. Once the graphite nozzle was inside the molten copper, copper oxide was added totaling 7.5 grams. The injection of CO/CuO was done over a ten minute time frame. After the 7.5 grams of CuO was injected, CO gas addition was continued for an additional ten minutes. When the additional ten minutes of CO gas injection was complete, the graphite nozzle was removed from the molten copper bath.

The reactor temperature was cooled to 1177°C at which time the molten copper was cast.

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Attachment 3: Continued

RO14 SOP 12.9A	*RO14 SOP - 12.9A Copper Pattern 5308379 Run Procedure*	
Normal Procedure	**Edited by:** ____________ **Reviewed by:** ____________ **Approved by:** ____________	

Purpose: To perform a run to duplicate pattern number 5308379 on copper

Safety and Environmental Precautions: Normal PPE
Electrical Safety Procedures

References:

Prerequisites: All parts and materials available before the run

STEP	ACTION

REACTOR SETUP

4) Wrap the alumina crucible with one layer of insulating paper.
5) Place the alumina crucible inside the reactor's containment vessel.
6) Place a two inch thick by 5 ½" round piece of high density duraboard in the centerline of the alumina crucible.
7) Place the graphite crucible (5 ½" O.D. * 4 ½" I. D. * 11 ½" tall course grain) in the centerline of the alumina crucible on top of the 2" duraboard.
8) Assemble the remaining sections of the reactor I.A.W. sop RO14 OP 4.0.

RUN PLAN

9) Ensure all general safety procedures are followed.

10) Verify the reactor is completely assembled and leak checked IAW RO14 SOP 4.1, RO14 SOP 5.0 and RO14 SOP 6.0.

11) Charge the reactor with 15 kg of 99.998% pure 20 PPM oxygen content copper through the ½" charging port.

12) Preheat the reactor to 1200 degrees C over a minimum of 12 hours.

CAUTION:
The 12 hours is required for proper thermal heat-up of the crucible.

13) Upon reaching 1200 degrees C, install the graphite lance into the molten bath while blowing CO gas at a rate of 5 LPM.

14) Immediately after the lance is installed, begin feeding 7.5 grams of copper oxide into the bath over a ten minute time frame.

15) After the copper oxide is added, continue to blow CO gas for an additional ten minutes.

16) After the ten minutes of additional co injection has been completed, immediately remove the gas injection lance.

17) Shutdown the Induction power supply.

18) Allow the bath temperature to decrease to 1065 degrees C.

19) Procedure to the quenching of the molten copper.

COPPER QUENCHING

20) Place two fire bricks at the bottom and in the centerline of the quench vessel.

21) Fill the quench vessel with 7" of tap water above the top surface of the fire bricks.

22) Disassemble the top end of the reactor by removing the top plate nuts and removing the top plate.

23) Don all appropriate PPE - silver suit, spates, silver head/face shield, heat gloves.

24) Lift the inner graphite crucible with two steel lifting tongs.

25) Lower the crucible into the quench vessel until the crucible is resting on the fire bricks.

26) As the water level decreases due to steam evaporation, replenish the water level to the 7" level.

27) Remove the graphite crucible from the quench vessel when the copper is at room temperature as indicated by the hand held micron temperature device.

****End of Procedure****

Attachment 4: Outside Lab XRF Analytical Protocols

An ARL 9800XP XRF was used to analyze the sample ingot. An ARL 9800XP is a sequential wavelength dispersive spectrometer (WDS). Specific emission lines are used to determine the presence or absence, and the concentrations of various elements. Each characteristic x-ray line is measured in sequence by the instrument by controlling the instrument geometry.

The WDS spectrometer relies on the fundamentals of x-ray diffraction, when x-ray fluorescence occurs when matter is bombarded by a stream of high-energy incident x-ray photons. When the incident x-radiation strikes the sample, the incident x-rays may be absorbed, scattered, or transmitted for the measurement of the fluorescent yield.

The ARL 9800XP utilizes an end-window rhodium (Rh) x-ray tube. The end window is composed of Be, and holds the tube at high vacuum. The filaments are heated giving off electrons by thermoionic emission. This beam of electrons then bombards the target Rh anode across a 10-70 keV voltage potential. Thus, primary x-rays are produced during the collision. The emitted x-ray spectrum consists of (1) "Continuum" or "Bremstrahlung" radiation, (2) characteristic x-ray lines of the target material (e.g., K and L series), and (3) characteristic lines from any contaminants. Thus, the primary spectrum appears as a series of sharp intense peaks arrayed over a broad hump of continuum radiation. The ARL is equipped with and uses two types of photon detectors, the Flow Proportional Counter (FPC).

The metal samples are prepared by cutting a cube shape (approximately 1.1875") from the center of the cooled ingot. An axial edge and a radial edge are denoted. To provide a smooth surface for analysis, the axial and radial faces are sequentially polished. The sample faces are sanded to 400 grit, then a polishing wheel is employed with 600 grit paper. Finally, a <1 μm polishing compound completes the smoothing process. Raw material samples were prepared by hydraulically pressing the material into a flat puck shape.

The sample is then cleaned with iso-propyl alcohol and placed in a sample cassette holder. The sample holder is then loaded into the XRF. The orientation of the detector crystal with respect to the sample and the photon detector is controlled synchronously such that characteristic x-ray lines can be accurately measured. A sequential measurement consists of positioning the diffraction crystal at a given theta (diffraction angle) and the detector at two-theta and counting for a given period of time. The crystal and detector are then rotated to a different angle for the next characteristic x-ray line.

The ARL 9800XP output from a scan is a graph of counts per second measured vs. two-theta angle.

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Attachment 5: Outside Lab XRF $K_{\alpha_{1,2}}$ scan protocols

Scans for Atomic Ordered Materials																
Scan Type	SCAN type	Crystal	Detector	start angle	Stop angle	increment	counting time (sec)	KV	mA	PBF	Eliptical Mask	Rotate	PHD counting Threshold	PHD Threshold mV	PHD window mV	Collimator	Environment
S	incremental	Ge111	FPC	109.7	111.7	0.02	5	40	60	none	2	yes	0	500	1200	fine	Vacuum

Attachment 6: Experimental Procedure for Copper Run 14-00-01

A cylindrical alumina-based crucible (89.07% Al_2O_3, 10.37% SiO_2, 0.16% TiO_2, 0.15% Fe_2O_3, 0.03% CaO, 0.01% MgO, 0.02% Na_2O_3, 0.02% K_2O; 9" O.D. x 7.75" I.D. x 14" depth) of a 100 pound induction furnace reactor supplied by Inductotherm, fitted with a 75-30R Powertrak power supply, was charged with 100 pounds copper (99.98% purity) through its charging port. During the entire procedure, a slight positive pressure of nitrogen (~0.5 psi) was maintained in the reactor using a continuous backspace purge. The reactor was heated to the metal charge liquidus point plus 300°F, at a rate no greater than 300°F/hour, as limited by the integrity of the crucible. The induction furnace operated in the frequence range of 0 kHz to 3000 kHz, with frequency determined by a temperature-controlled feedback loop implementing an Omega Model CN300 temperature controller.

The temperature was again increased to 2462°F again using a rate no greater than 300°F/hour. When this temperature was reached, graphite saturation assemblies (3/8" OD, 36" long high purity (<5 ppm impurities) graphite rods) were inserted to the bottom of the copper charge through ports located in the top plate. The copper was held at 2462°F for 4 hours. Every 30 minutes during the hold period, an attempt was made to lower the graphite saturation assemblies as dissolution occurred. As the copper became saturated with carbon, the graphite saturation assemblies were consumed. After the 4 hour hold period was complete, the graphite saturation assemblies were removed.

The reactor temperature was increased to 2480°F over 7 minutes. The temperature was then varied between 2480°F and 2530°F for 15 cycles. Each cycle consisted of raising the temperature continuously over 7 minutes and lowering the temperature continuously over 7 minutes. After the 15 cycles were completed, a gas addition lance was lowered into the molten metal to a position approximately 2" from the bottom of the reactor and a 1.5 L/min flow of argon was begun. The temperature of the copper was varied over another 5 cycles between 2480°F and 2530°F.

After the fifth cycle, the reactor temperature was lowered to 2462°F over a 10 minute period with continued argon addition. The graphite saturation assemblies were reinstalled in the copper and remained there for 1 hour. The graphite saturation assemblies were removed.

The reactor temperature was lowered to 2459°F over 5 minutes. The reactor was held at this temperature for 5 minutes with continued argon addition. The temperature was then varied between 2459°F and 2453°F over 20 cycles. Each cycle consisted of lowering the temperature continuously over 9 minutes and raising the temperature continuously over 9 minutes. The argon addition ceased after completion of the 20 cycles.

The reactor temperature was lowered to 2450°F over 5 minutes. The temperature was varied between 2450°F and 2441°F over 4 ½ cycles. Each cycle consisted of lowering the temperature continuously over 5 minutes and raising the temperature continuously over 3 minutes. In addition, while raising the temperature, a 1.5 L/min flow of argon was added, and while lowering the temperature, a 1.5 L/min flow of nitrogen was added.

The reactor temperature was lowered to 2438°F over 5 minutes. The temperature was varied between 2438°F and 2406°F for 15.5 cycles. Each cycle consisted of lowering the temperature continuously over 15 minutes and raising the temperature continuously over 15 minutes. In addition, while raising the temperature, a 1.5 L/min flow of argon was added, and while lowering the temperature, a 1.5 L/min flow of nitrogen was added. All gas addition, except for the purge of nitrogen ceased after the 15.5 cycles were completed.

The temperature was varied between 2406°F and 2419°F for one cycle. The cycle consisted of raising the temperature continuously over 15 minutes and lowering the temperature continuously over 15 minutes. The gas addition lance was removed.

The reactor temperature was rapidly cooled by quenching in water, so that the copper solidified into an ingot.

Attachment 7: Experimental Procedure for Copper Run 14-00-03

A cylindrical alumina-based crucible (89.07% Al_2O_3, 10.37% SiO_2, 0.16% TiO_2, 0.15% Fe_2O_3, 0.03% CaO, 0.01% MgO, 0.02% Na_2O_3, 0.02% K_2O; 9" O.D. x 7.75" I.D. x 14" depth) of a 100 pound induction furnace reactor supplied by Inductotherm, fitted with a 75-30R Powertrak power supply and was charged with 100 pounds copper (99.98% purity) through its charging port. During the entire procedure, a slight positive pressure of nitrogen (~0.5 psi) was maintained in the reactor using a continuous backspace purge. The reactor was heated to the metal charge liquidus point plus 300°F, at a rate no greater than 300°F/hour, as limited by the integrity of the crucible. The induction furnace operated in the frequence range of 0 kHz to 3000 kHz, with frequency determined by a temperature-controlled feedback loop implementing an Omega Model CN300 temperature controller.

The temperature was again increased to 2462°F again using a rate no greater than 300°F/hour. When this temperature was reached, graphite saturation assemblies (3/8" OD, 36" long high purity (<5 ppm impurities) graphite rods) were inserted to the bottom of the copper charge through ports located in the top plate. The copper was held at 2462°F for 4 hours. Every 30 minutes during the hold period, an attempt was made to lower the graphite saturation assemblies as dissolution occurred. As the copper became saturated with carbon, the graphite saturation assemblies were consumed. After the 4 hour hold period was complete, the graphite saturation assemblies were removed.

The reactor temperature was increased to 2480°F over 7 minutes. The temperature was then varied between 2480°F and 2530°F for 15 cycles. Each cycle consisted of raising the temperature continuously over 7 minutes and lowering the temperature continuously over 7 minutes. After the 15 cycles were completed, a gas addition lance was lowered into the molten metal to a position approximately 2" from the bottom of the reactor and a 1.5 L/min flow of argon was begun. The temperature of the copper was varied over another 5 cycles between 2480°F and 2530°F.

After the fifth cycle, the reactor temperature was lowered to 2462°F over a 10 minute period with continued argon addition. The graphite saturation assemblies were reinstalled in the copper and remained there for 1 hour. The graphite saturation assemblies were removed.

The reactor temperature was lowered to 2459°F over 5 minutes. The reactor was held at this temperature for 5 minutes with continued argon addition. The temperature was then varied between 2459°F and 2453°F over 20 cycles. Each cycle consisted of lowering the temperature continuously over 9 minutes and raising the temperature continuously over 9 minutes. The argon addition ceased after completion of the 20 cycles.

The reactor temperature was lowered to 2450°F over 5 minutes. The temperature was varied between 2450°F and 2441°F over 4 ½ cycles. Each cycle consisted of lowering the temperature continuously over 5 minutes and raising the temperature continuously over 3 minutes. In addition, while raising the temperature, a 1.5 L/min flow of argon was added, and while lowering the temperature, a 1.5 L/min flow of nitrogen was added.

The reactor temperature was lowered to 2438°F over 5 minutes. The temperature was varied between 2438°F and 2406°F for 15.5 cycles. Each cycle consisted of lowering the temperature continuously over 15 minutes and raising the temperature continuously over 15 minutes. In addition, while raising the temperature, a 1.5 L/min flow of argon was added, and while lowering the temperature, a 1.5 L/min flow of nitrogen was added. All gas addition, except for the purge of nitrogen ceased after the 15.5 cycles were completed.

The temperature was varied between 2406°F and 2419°F for one cycle. The cycle consisted of raising the temperature continuously over 15 minutes and lowering the temperature continuously over 15 minutes. The gas addition lance was removed.

The reactor temperature was rapidly cooled by quenching in water, so that the copper solidified into an ingot.